Angular-Momentum Conditions for a Correlated Wavefunction

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Citation: The Journal of Chemical Physics **43**, 1605 (1965); doi: 10.1063/1.1696978
View online: http://dx.doi.org/10.1063/1.1696978
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/43/5?ver=pdfcov
Published by the AIP Publishing

where q^2 is the vibrational coordinate, p_2 its conjugate momentum, and integration at the given q^1-coordinate hypersurface is over a vibrational period. The vibrational energy equals $J\nu$, so that for a vibrationally adiabatic motion a portion of this energy, $J(\nu^\ddagger - \nu_0)$, must go into translational energy along q^1, where $\nu^\ddagger$ is the value of vibration frequency at the saddle point and ν_0 is that for the reactants. In the two calculations of Wall *et al.*, cited above, J equaled $\frac{1}{2}h$ and $\frac{3}{2}h$, respectively.[15a]

It is possible, with the aid of analytical mechanics, to make a calculation of this tendency of λ (quantum mechanics) or J (classical mechanics) to be constant for the vibrational motion. Some calculations of this nature are now in progress.[16]

Wall, Hiller, and Mazur have also made numerical calculations on classical-mechanical transmission coefficients for the case of rotating systems.[17] In this case the simple results described above for conversion of vibrational energy to energy useful for overcoming the barrier were apparently not obtained [see, however, Ref. 15(a)]. It may be noted that in the activated-complex expression given by Eq. (15) vibrational adiabaticity was assumed only in the immediate vicinity of the activated complex, and not for all values of q^1 from region of reactants to that of products.

[15a] *Note added in proof:* Further numerical calculations of trajectories in this system (with a different potential-energy surface) support this vibrational adiabaticity suggestion, not only for the rotation-free system but also, in contrast with earlier work, for the rotation-present one [M. Karplus, R. N. Porter, and R. D. Sharma (private communication)].

[16] R. A. Marcus (unpublished results).

[17] F. T. Wall, L. A. Hiller, Jr., and J. Mazur, J. Chem. Phys. **35**, 1284 (1961).

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 43, NUMBER 5 1 SEPTEMBER 1965

Angular-Momentum Conditions for a Correlated Wavefunction

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(Received 21 April 1965)

We obtain the conditions under which a correlation wavefunction containing pair correlation functions for the $2p^n$ electrons of C(^3P, ^1D, ^1S), N(^4S), O(^3P), and Ne will be an eigenfunction of the orbital and spin angular-momentum operators. These pair functions contain quite general powers of electronic and interelectronic coordinates along with their variational parameters and should avoid the convergence difficulties of configuration interaction. In all these cases, except carbon which has just one pair of $2p$ electrons, one cannot obtain such a pair function, $\hat{u}_{ij}^{(1)}$, just by minimizing its pair energy, $\bar{\epsilon}_{ij}^{(1)}$, alone; i.e., minimizing the variational parameters of a $\hat{u}_{ij}^{(1)}$. Minimization of one pair at a time corresponds to working with just a part of the correlation wavefunction which by itself cannot converge to the right symmetry state. One must minimize sums of pair energies by taking a correlation wavefunction containing enough pair functions so as to have the right symmetry. The sets of variational parameters in these different $\hat{u}_{ij}$'s are not independent but are coupled. These symmetry requirements now make the determination of pair correlation functions quite a bit more difficult. In carbon (^3P), these conditions do not apply, but the $\hat{u}_{ij}^{(1)}$ of the $2p^2$ electrons of the ^1D multiplet must be made orthogonal to the unoccupied orbitals of the open shell if it is to contain general powers of the interelectronic coordinate. This is in addition to the required orthogonality to occupied orbitals. We also obtain a form of the correlation wavefunction for $2p^2(^1S)$, a nonsingle-determinant Hartree–Fock (HF) state. This has not been previously known. We do this by applying the angular momentum stepdown operator to the correlation wavefunctions of multiplet states with single Slater determinant HF states and studying the resulting forms of the correlation wavefunction which, in turn, belong to some nonsingle-determinant states of these multiplets.

INTRODUCTION

A MANY-electron wavefunction contains a Hartree–Fock and a correlation part. This total wavefunction must be an eigenfunction of all operators that commute with the Hamiltonian; e.g., orbital (L^2) and spin (S^2) angular momentum of an atom. An approximate many-electron wavefunction will not, in general, be a simultaneous eigenfunction of all these commuting operators. Such wavefunctions are still useful for they may give good expectation values for many of these operators. Those operators, e.g., L^2, S^2, whose eigenvalues specify the symmetry of a state are particularly important. For example, in the variational determination of an approximate wavefunction, we must specify the symmetry properties of a trial function even before obtaining the expectation value of the Hamiltonian. This is clearly better than having to project out the desired symmetry component from a wavefunction of indefinite symmetry.

For an atomic system, it is quite simple to make the Hartree–Fock wavefunction an eigenfunction of L^2 and S^2, since its transformation properties depend

* Contribution No. 3234.

on those of the angular parts of its one-electron functions. These, in turn, are the spherical harmonics. To make the correlation part of the wavefunction an eigenfunction of L^2 and S^2 is a bit more difficult. This part of the wavefunction will contain the complicated dependence of the wavefunction on the relative coordinates of its electrons, but still the electrons must "move" so as to preserve always the over-all symmetry of the system. This is pointed out, or at least assumed, in the formalism of theories of electron correlation. Not much has been done explicitly on the angular momentum properties of the correlation wavefunction itself.[1]

In this paper, we study the angular-momentum properties, L^2, S^2, L_z, S_z, of the correlation wavefunction. We specifically choose a correlation wavefunction containing powers of electronic and interelectronic coordinates. This avoids the slow convergence of a configuration interaction (CI) expansion. Although our methods are applicable to other theories[2] which introduce relative coordinates into the wavefunction, we here apply them to Sinanoğlu's theory of electron correlation.[3] Sinanoğlu has developed a scheme that gives the correlation wavefunction. Pair correlations are the most important part of this correlation wavefunction, and the final form of the theory gives convenient variational expressions for obtaining these pair correlation functions and energies. The equations are valid for closed-shell systems and those non closed-shell systems with a single Slater determinant Hartree–Fock (HF) wavefunction.

We derive the conditions under which a correlation wavefunction containing pair functions for the $2p$ electrons of carbon (^3P, ^1D), N(^4S), O(^3P), and Ne will be an eigenfunction of L^2 and S^2. These pair functions contain quite general powers of electronic and interelectronic coordinates with their variational parameters. Only pair functions in the open shell are of interest here. These functions are general enough to answer the questions we ask; and this is what matters, i.e., whether the variational parameters of one pair function can be varied independently of those in another and still give a correlation wavefunction with the right angular momentum properties. With the exception of carbon (^3P) with only two $2p$ electrons, the answer is no. Many such parameters in a particular pair function are coupled to corresponding ones in other pair functions. This implies that a pair energy cannot be found by separate minimization of its pair function, for these cannot be varied independently. Such correlated pair functions are coupled. If they are varied independently, the resulting function will not have the proper symmetry and cannot converge to the correct electronic state. One must then minimize sums of pair energies at a time. This corresponds to including as many pair functions as necessary so as to give a correlation wavefunction of proper symmetry. One now has fewer independent variational parameters.

In the next section, we show how these results come about through examples: (a) For $2p^2$ correlation in C(^3P), there is only one pair function, and angular momentum properties are easily satisfied. For the more interesting case of $2p^2$ correlation in C(^1D), i.e., a "tight" $2p$ pair, symmetry conditions impose some restrictions on the choice of a correlated pair function. Either some powers of the interelectronic coordinate must be omitted or else some additional orthogonality requirements introduced, i.e., orthogonality to unoccupied orbitals of the open shell. (b) The ^1S multiplet of carbon does not have a single-determinant HF. We can infer the form of its correlation wavefunction by examining the form of the correlation wavefunctions for those nonsingle-determinant HF states of the ^3P and $^1D(M_L=0, M_S=0)$ multiplets. We get these by applying the angular momentum stepdown operator to the correlation wavefunctions for those single-determinant HF states of ^3P and ^1D multiplets. (c) For $2p_{+1}\alpha 2p_{-1}\alpha 2p_0\alpha(^4S)$ of nitrogen, only the sum of pair energies for all interactions, i.e., $\epsilon(p_{+1}p_{-1})+\epsilon(p_{+1}p_0)+\epsilon(p_{-1}p_0)$, can be minimized if we are to get a ^4S correlation wavefunction with interelectronic coordinates in it. There is only one independent set of variational parameters here. (d) For O(^3P), Ne(^1S), results similar to those in (c) hold. We give particular attention to Ne(^1S). Many of the pair energies in $2p^6$ correlation, although not "independent", will still be equal. This gives some simplification.

THEORY AND RESULTS

For clarity, we give some of Sinanoğlu's equations[3] along with our arguments. The exact wavefunction of a many-electron system can be written as

$$\psi=\phi_0+\chi, \tag{1}$$

where ϕ_0 is the HF wavefunction and χ the correlation part. Take ϕ_0 and χ so that

$$\langle\phi_0, \chi\rangle=0. \tag{2}$$

The total wavefunction, ψ, must be an eigenfunction of all operators that commute with the Hamiltonian. From this and Eq. (2), we have for an atom:

$$L^2\phi_0=L(L+1)\phi_0, \tag{3a}$$

$$L^2\chi=L(L+1)\chi. \tag{3b}$$

This holds for other operators, e.g., S^2. No matter how and to what accuracy we get χ, it should satisfy Eq. (3b). The most important part of χ comes from pair correlations (double excitations of configuration interaction), i.e., the first-order wavefunction of

[1] But, for spin properties in Be, see H. Levine, M. Geller, and H. Taylor, J. Chem. Phys. **40**, 595 (1964).

[2] See for example, L. Szász, Phys. Rev. **126**, 169 (1962); and V. Fock, M. Veselov, and M. Petrashen, Zh. Eksperim. i Teor. Fiz. **10**, 723 (1940).

[3] For a review and references to earlier papers see O. Sinanoğlu, Advan. Chem. Phys. **6**, 315 (1964).

Rayleigh–Schrödinger (RS) perturbation theory. Our results could be extended to apply to the better approximations to χ.

Let H be the total Hamiltonian, H_0 the HF Hamiltonian, $H=H_0+H_1$, and $E_n=\langle\phi_0, H_n\phi_0\rangle$ $(n=0, 1)$. The differential equation for the first-order wavefunction χ_1 of RS perturbation theory is

$$(H_0-E_0)\chi_1=(E_1-H_1)\phi_0. \tag{4}$$

Solving Eq. (4) directly, something we usually cannot do, will always give a χ_1 that satisfies Eq. (3b), since perturbation-theory wavefunctions of any order automatically satisfy the same symmetry as the zeroth-order wavefunction ϕ_0 [see Eq. (3a)]. But we can obtain an approximate solution to Eq. (4) by picking a variational form of χ_1 and varying $\tilde{\chi}_1$ in Eq. (5):

$$E_2\leq 2\langle\phi_0, (H_1-E_1)\tilde{\chi}_1\rangle+\langle\tilde{\chi}_1, (H_0-E_0)\tilde{\chi}_1\rangle. \tag{5}$$

Equation (5) is the variational principle for the second-order energy E_2.

To use Eq. (5) we must pick a $\tilde{\chi}_1$ with the correct symmetry. Equation (5) cannot select the right symmetry component on its own. To see this, pick a $\tilde{\chi}_1$ that does not satisfy Eq. (3b). With a self-adjoint projection operator O get a $\tilde{\chi}_1{}^s$ that does:

$$\tilde{\chi}_1{}^s=O\tilde{\chi}_1. \tag{6}$$

Put $O\tilde{\chi}_1$ in Eq. (5). Since $O^2=O$, the commutator $[H_0O]=0$, and both operators are self adjoint (H_0O is then Hermitian), we get

$$E_2\leq 2\langle\phi_0, (H_1-E_1)\tilde{\chi}_1\rangle+\langle\tilde{\chi}_1, (H_0-E_0)O\tilde{\chi}_1\rangle. \tag{7}$$

Equation (7) only equals Eq. (5) if $\tilde{\chi}_1{}^s=\tilde{\chi}_1=O\tilde{\chi}_1$, i.e., $\tilde{\chi}_1$ is already symmetry adapted.

With a single-determinant ϕ_0, either by operator techniques[3] or otherwise, one obtains

$$\chi_1=\sum_{i>j}(A/\sqrt{2})\{(1, 2, 3, \cdots, N)(\hat{u}_{ij}{}^{(1)}/(ij))\}, \tag{8}$$

where A is the N-electron antisymmetrizer, $1, 2, \cdots, N$ are HF spin orbitals, and $\hat{u}_{ij}{}^{(1)}$ is the first-order pair correlation function for electrons in Orbitals i and j. The function $\hat{u}_{ij}{}^{(1)}$ can contain interelectronic coordinates but must be orthogonal to all occupied HF orbitals. Equation (8) holds for closed-shell and non-closed-shell single-determinant HF systems.[3] Put $\tilde{\chi}_1$ Eq. (8) into Eq. (5) and $\tilde{E}_2=\sum_{i>j}\tilde{\epsilon}_{ij}{}^{(2)}$, where (see Ref. 3)

$$\tilde{\epsilon}_{ij}{}^{(2)}\leq 2\langle B(ij), g_{ij}\hat{u}_{ij}{}^{(1)}\rangle+\langle\hat{u}_{ij}{}^{(1)}, (e_i+e_j)\hat{u}_{ij}{}^{(1)}\rangle, \tag{9}$$

B is the two-electron antisymmetrizer, $g_{ij}=r_{ij}{}^{-1}$, and

$$e_i=h_i{}^0+V_i-\epsilon_i. \tag{10}$$

$h_i{}^0$ is the bare-nuclei Hamiltonian, V_i the Hartree–Fock potential, and ϵ_i an orbital energy. Formally, variation of each $\hat{u}_{ij}{}^{(1)}$, i.e., of its variational parameters, will give an $\tilde{\epsilon}_{ij}{}^{(2)}$. Each $\hat{u}_{ij}{}^{(1)}$ goes back into Eq. (8) to give an over-all $\tilde{\chi}_1$. This $\tilde{\chi}_1$ must satisfy Eq. (3b). If, for arbitrary values of the variational parameters in each $\hat{u}_{ij}{}^{(1)}$, $\tilde{\chi}_1$ satisfies Eq. (3b), then each $\hat{u}_{ij}{}^{(1)}$ can be varied independently. But what if the sets of variational parameters in, say, $\hat{u}_{ij}{}^{(1)}$ and $\hat{u}_{kl}{}^{(1)}$ must be equal to have $\tilde{\chi}_1$ satisfy Eq. (3b)? Then $(\tilde{\epsilon}_{ij}{}^{(2)}+\tilde{\epsilon}_{kl}{}^{(2)})$ must be minimized together so that throughout the variation $\tilde{\chi}_1$ satisfies Eq. (3b). Neither $\tilde{\epsilon}_{ij}{}^{(2)}$ nor $\tilde{\epsilon}_{kl}{}^{(2)}$ has an 'independent" variational expression. This is the type of question we try to answer for $2p$ correlation in the first-row atoms.

We choose to study $\hat{u}_{ij}$'s containing interelectronic coordinates. Although it is not the most general, it is certainly of great interest computationally. To get such a $\hat{u}_{ij}{}^{(1)}$, take a correlated two-electron function[3] ψ_{ij},

$$\psi_{ij}(1, 2)=B[\phi_i(1)\phi_j(2)]\{\sum_k[\beta_k(r_1+r_2)^{m_k}+\alpha_k r_{12}{}^{n_k}]\}. \tag{11}$$

This is representative enough to prove our point. Obtain a $u_{ij}{}^0$ such that

$$u_{ij}{}^0=(1/c)\psi_{ij}-B(\phi_i\phi_j) \tag{12}$$

with $\langle u_{ij}{}^0, B(\phi_i{}^*\phi_j{}^*)\rangle=0$ and $c=\langle\psi_{ij}{}^*, B(\phi_i\phi_j)\rangle$. Next orthogonalize $u_{ij}{}^0$ to all occupied HF orbitals through the projection operator Q; i.e., $\hat{u}_{ij}=Qu_{ij}{}^0$ with

$$Qu_{ij}{}^0=u_{ij}{}^0-\sqrt{2}\sum_k B\{\phi_k>\langle\phi_k{}^*, u_{ij}{}^0\rangle\}+\sum_{k>l}B(\phi_k\phi_l)>\langle B(\phi_k{}^*\phi_l{}^*), u_{ij}{}^0\rangle. \tag{13}$$

Let us look at such $\hat{u}_{ij}$'s for the $2p$ electrons in $C(^3P, ^1D)$, $N(^4S)$, $O(^3P)$, and $Ne(^1S)$.

CARBON: ^3P, ^1D, ^1S MULTIPLETS

This is the simplest case of $2p$ correlation. For the ^3P multiplet, take a single-determinant HF state $(M_L=1, M_S=1)$ and construct the $2p^2$ pair function,[4] $\hat{u}^{(1)}(2p_{+1}2p_0)$ [Eqs. (12) and (13)]. Applying L^2 and S^2 to this, we see that $\hat{u}^{(1)}(p_{+1}p_0)$ can contain any β_k, m_k, α_k, and n_k [Eq. (11)]. Equation (13) contains many terms, but most of them vanish through antisymmetry when we form $\tilde{\chi}$.

The $2p^2$ correlation in the ^1D multiplet $(M_L=2, M_S=0)$, i.e., "tight $2p^2$" correlation is of more interest here. Here we give our results in a condensed form as the derivation is straightforward. Form a $\tilde{\chi}_1$ containing $\hat{u}^{(1)}(2p_{+1}\alpha 2p_{+1}\beta)$. Applying L^2 to this, we see that it is not an angular momentum eigenfunction. To have it an eigenfunction of L^2, $\hat{u}^{(1)}(2p_{+1}\alpha 2p_{+1}\beta)$ can contain arbitrary β_k, m_k, but only the $r_{12}{}^2$ interelectronic term,[5] e.g., αr_{12} may not be used. To avoid this restriction

[4] This is the only $\hat{u}_{ij}{}^1$ of interest here since it lies in the open shell. Others can be included, e.g., for $\hat{u}(2s^2)$ in B, C, N, and Ne, see V. McKoy and O. Sinanoğlu, J. Chem. Phys. 41, 2689 (1964).

[5] It may contain higher even powers of r_{12}. Note that with $r_{12}{}^2$ we introduce $\cos\theta_{12}$ into the wavefunction, since $r_{12}{}^2=r_1{}^2+r_2{}^2-2r_1r_2\cos\theta_{12}$.

to just the $\alpha_k r_{12}^2$ term [Eq. (11)], we apply a projection operator to the more general $\tilde{\chi}_1$ containing arbitrary powers of r_{12}. The result is that $\hat{u}(p_{+1}\alpha p_{+1}\beta)$ can contain arbitrary powers of r_{12} but the $\hat{u}_{ij}^0$ used to get $\hat{u}_{ij}^{(1)}$ [see Eq. (12)] must be orthogonalized not only to the occupied orbitals i.e., the usual exclusion effect, but also to the unoccupied orbitals of the open shell. The new terms are introduced by the projection operator but then seem to correspond to these additional orthogonalizations to the unoccupied orbitals. Here a symmetry requirement is equivalent to an orthogonality condition.

The ^1S multiplet of carbon does not have a single-determinant HF state. We do not know how to write a correlation wavefunction for this state. Here we see that with the angular-momentum step-up and step-down operators one obtains a $\tilde{\chi}_1$ for this multiplet. Take the $\tilde{\chi}_1$'s belonging to the single-determinant states of the ^3P and ^1D multiplets and to these apply the step-down operators to get the $\tilde{\chi}_1$'s belonging to the $^3P(M_L=0,\ M_S=0)$ and $^1D(M_L=0,\ M_S=0)$ multiplet states. But for a $(2p)^2$ configuration there are only three possible $\tilde{\chi}_1$'s with $M_L=0$, $M_S=0$, and they must be orthogonal. We already have the form of two of these. The third one must be of ^1S symmetry to be orthogonal to the other two, and it belongs to the ^1S multiplet of carbon. Ladder operators have been used this way in ordinary multiplet theory. The analysis here is quite long, so we just state the result.

With these methods, the correlation wavefunction of ^1S multiplet has the form

$$\tilde{\chi}(^1S) = (1/\sqrt{2})\{A[1s^2 2s^2 \hat{u}^{(1)}(p_{+1}\alpha p_{-1}\beta)] + A[1s^2 2s^2 \hat{u}^{(1)}(p_{-1}\alpha p_{+1}\beta)] - A[1s^2 2s_2 \hat{u}^{(1)}(p_0\alpha p_0\beta)]\}. \quad (14)$$

The functions $\hat{u}^{(1)}(k, l)$, [Eq. (14)], are constructed just as we did for the $\hat{u}_{ij}$'s of a single-determinant HF system, but each $\hat{u}^{(1)}(k, l)$ is orthogonal to all the HF orbitals of its ϕ_0 and not just to those in "its" Slater determinant. The $\hat{u}^{(1)}(k, l)$'s have the same variational parameters. These ladder operators have not been previously used to study the correlation wavefunction. With these equations one may try to see how $2p^2(^1S)$ correlation is related to the conceptually simpler $2p_{+1}\alpha 2p_{+1}\beta(^1D)$ correlation.

NITROGEN (^4S) AND OXYGEN (^3P)

These multiplets of $N(2p^3)$ and $O(2p^4)$ have single-determinant HF's:

$$\phi_0(2p^3, {}^4S) = A(1s^2 2s^2 2p_{+1}\alpha 2p_{-1}\alpha 2p_0\alpha), \quad (15a)$$

$$\phi_0(2p^4, {}^3P) = A(1s^2 2s^2 2p_{+1}\alpha 2p_{+1}\beta 2p_{-1}\alpha 2p_0\alpha). \quad (15b)$$

Consider the $2p^3$ system. There are three pair functions in the open shell, and the $\tilde{\chi}_1$, Eq. (8), is

$$\tilde{\chi}_1 = (1/\sqrt{2})\{A[1s^2 2s^2 \hat{u}(p_{+1}\alpha p_{-1}\alpha)\, p_0\alpha] - A[1s^2 2s^2 \hat{u}(p_{+1}\alpha p_0\alpha)\, p_{-1}] + A[1s^2 2s^2 \hat{u}(p_{-1}p_0)\, p_{+1}]\}, \quad (16)$$

with $\tilde{\chi}_1$, Eq. (16), $\tilde{E}_2$, Eq. (5), is

$$\tilde{E}_2 \leq \tilde{\epsilon}^{(2)}(p_{+1}\alpha p_{-1}\alpha) + \tilde{\epsilon}^{(2)}(p_{+1}\alpha p_0\alpha) + \tilde{\epsilon}^{(2)}(p_{-1}\alpha p_0\alpha), \quad (17)$$

where each $\tilde{\epsilon}^{(2)}(p_m p_n)$ is defined by Eq. (9). The total $\tilde{\chi}_1$ must satisfy Eq. (3b). Each $\tilde{\epsilon}_{ij}^{(2)}$ term of Eq. (17) can be found by separate minimization of its $\hat{u}_{ij}^{(1)}$, i.e., one pair at a time, provided this corresponds to minimizing a part of $\tilde{\chi}_1$ that by itself satisfies the angular momentum condition, Eq. (3b). The function $\tilde{\chi}_1$ will then converge to the right electronic state. We are interested in a $\hat{u}_{ij}^{(1)}$ constructed from a correlated two-electron function such as Eq. (11). We now show that with such correlated $\hat{u}_{ij}^{(1)}$'s, only the complete $\tilde{\chi}_1$, Eq. (16), satisfies Eq. (3b). No term in Eq. (16) by itself satisfies Eq. (3b). Below, we see how this comes about and what it implies.

With Eqs. (11) to (13), construct the three $\hat{u}_{ij}^{(1)}$'s and put them into $\tilde{\chi}_1$, Eq. (16). Many terms vanish through antisymmetry, but the expression still contains too many terms to write out in full. We only display that term of $\tilde{\chi}_1$ coming from the $(1/c)\psi_{ij}$ part of $\hat{u}_{ij}$ [see Eq. (12)]. There are three such terms, one each from the $\hat{u}(p_{+1}p_{-1})$, $\hat{u}(p_{+1}p_0)$ and $\hat{u}(p_{-1}p_0)$ parts of $\tilde{\chi}_1$:

$$(A/c_1)\{2p_{+1}(1)\alpha(1)\,2p_{-1}(2)\alpha(2) \times[\sum_k \beta_k(r_1+r_2)^{m_k}+\alpha_k r_{12}^{n_k}]2p_0(3)\alpha(3)\}, \quad (18a)$$

$$-(A/c_2)\{2p_{+1}(1)\alpha(1)\,2p_0(2)\alpha(2) \times[\sum_k \beta_k(r_1+r_2)^{m_k}+\alpha_k r_{12}^{n_k}]2p_{-1}(3)\alpha(3)\}, \quad (18b)$$

$$+(A/c_3)\{2p_{-1}(1)\alpha(1)\,2p_0(2)\alpha(2) \times[\sum_k \beta_k(r_1+r_2)^{m_k}+\alpha_k r_{12}^{n_k}]2p_{+1}(3)\alpha(3)\}. \quad (18c)$$

The coordinates 1, 2, and 3 are in the same order throughout Eqs. (18). This is always possible through permutations. None of these terms is an eigenfunction of L^2. Neither are many of the remaining terms in $\tilde{\chi}$, which we have not written out. For example, apply L^2 to Eq. (18a). With $f_i(r_1, r_2, r_{12}) = \sum_k \beta_{ik}(r_1+r_2)^{m_{ik}}+\alpha_{ik}r_{12}^{n_{ik}}$, this gives

$$\left\{\frac{4A}{c_1}[2p_{+1}(1)\alpha(1)\,2p_{-1}(2)\alpha(2)f_1(r_1, r_2, r_{12})\,2p_0(3)] + \frac{2A}{c_2}[2p_0(1)\alpha(1)\,2p_{-1}(2)\alpha(2)f_2(r_1, r_2, r_{12})\,2p_{+1}(3)\alpha(3)] + \frac{2A}{c_3}[2p_{+1}(1)\alpha(1)\,2p_0(3)\alpha(3)f_3(r_1, r_2, r_{12})\,2p_{-1}(3)\alpha(3)]\right\}. \quad (19)$$

Applying L^2 to Eqs. (18a) to (18c), we see that only the sum of these is an eigenfunction of L^2, and the three sets of variational parameters $\{\beta_{ik}/c_i, \alpha_{ik}/c_i\}$ must be equal for this to be so. This condition also makes the remaining terms of $\tilde{\chi}_1$ an eigenfunction of L^2. This means that we can only minimize the sum of these pair energies as there is only one set, $\{\beta_{ik}/c_i, \alpha_{ik}/c_i\}$, of independent variational parameters. Variation of a part of $\tilde{\chi}_1$, say, one pair function at a time, will not converge to the correct state. Such pairs are coupled through the angular-momentum requirements of the total wavefunction. If all the $\bar{\epsilon}_{ij}$'s were equal, this would simplify the equations.

With correlated pair functions for $2p^3$ system, the pair functions are coupled. The very same results hold for $O(^3P)$, but now there are six pair energies. Those for antiparallel spin correlation will, of course, be much larger than the parallel spin correlations. In the next section, we see that L^2 conditions can be satisfied by two parts of $\tilde{\chi}_1$ separately, one for antiparallel and another for parallel spin correlations. But S^2 conditions recouple them. This will be less serious than coupling through L^2 requirements.

Ne: $(2p^6)$

For neon, we write a correlation wavefunction containing all the pair correlation functions for the six $2p$ electrons. Again these are correlated $\hat{u}_{ij}$'s constructed from a correlated two-electron function of the type Eq. (11). Each has a set of variational parameters. Nine of the 15 pair functions correspond to antiparallel spin correlations and six to parallel spin correlations. Each $\hat{u}_{ij}^{(1)}$ can be found through separate minimization of its pair energy $\bar{\epsilon}_{ij}^{(2)}$, Eq. (9), only if this corresponds to taking a term in $\tilde{\chi}_1$, Eq. (8), that by itself satisfies all the symmetry requirements. We show that there is no single $\hat{u}_{ij}$ satisfying this requirement. To satisfy L^2, L_z, S_z, we must take a $\tilde{\chi}_1$ containing either all nine antiparallel spin pair correlation functions or six parallel spin $\hat{u}_{ij}$'s. To make $\tilde{\chi}_1$ an eigenfunction of S^2, in addition to L^2 L_z^2, and S_z it must contain all 15 $\hat{u}_{ij}$'s. This last coupling will be less important since the antiparallel spin-pair energies will be much larger than the parallel spin-pair energies.

The expressions contain very many terms, and we only give a few of these as we did for the $2p^3$ configuration. Note that we use a pair function $\hat{u}_{ij}$ in which i and j refer to occupied HF orbitals ϕ_i and ϕ_j. These are called unique pairs.[3] We only display those terms of $\tilde{\chi}_1$ coming from the $(1/c)\psi_{ij}$ parts of the $\hat{u}_{ij}$'s [see Eq. (12)]. The conditions required to make this combination of terms an eigenfunction of L^2 are just sufficient to make the remaining terms of $\tilde{\chi}_1$ an eigenfunction of L^2. Let $f_i(r_1, r_2, r_{12}) = \sum_k[\beta_{ki}(r_1+r_2)^{m_{ki}}+\alpha_{ki}r_{12}^{n_{ki}}]$. The functions $f_i(r_1, r_2, r_{12})$ may all be different if their variational parameters are independent. The c_i's are functions of the variational parameters. Omitting the $1s^22s^2$ core for convenience, and with electrons labeled 1 to 6, the following group of terms is the smallest that could be made an eigenfunction[6] of L^2. This group of terms,

$$\begin{aligned}\{&A[p_{+1}\bar{p}_{+1}p_{-1}\bar{p}_{-1}p_0(5)\bar{p}_0(6)f_1(r_5, r_6, r_{56})c_1^{-1}]\\ &+A[p_0\bar{p}_0p_{-1}\bar{p}_{-1}p_{+1}(5)\bar{p}_{+1}(6)f_2(r_5, r_6, r_{56})c_2^{-1}]\\ &+A[p_{+1}\bar{p}_{+1}p_0\bar{p}_0p_{-1}(5)p_{-1}(6)f_3(r_5, r_6, r_{56})c_3^{-1}]\\ &+A[p_0\bar{p}_{-1}p_{+1}\bar{p}_0p_{-1}(5)\bar{p}_{+1}(6)f_4(r_5, r_6, r_{56})c_4^{-1}]\\ &+A[p_{-1}\bar{p}_0p_0\bar{p}_{+1}p_{+1}(5)\bar{p}_{-1}(6)f_5(r_5, r_6, r_{56})c_5^{-1}]\\ &+A[p_{+1}\bar{p}_{-1}p_{-1}\bar{p}_0p_0(5)\bar{p}_{+1}(6)f_6(r_5, r_6, r_{56})c_6^{-1}]\\ &+A[p_{-1}\bar{p}_{+1}p_{+1}\bar{p}_0p_0(5)\bar{p}_{-1}(6)f_7(r_5, r_6, r_{56})c_7^{-1}]\\ &+A[p_0\bar{p}_{-1}p_{-1}\bar{p}_{+1}p_{+1}(5)\bar{p}_0(6)f_8(r_5, r_6, r_{56})c_8^{-1}]\\ &+A[p_0\bar{p}_{+1}p_{+1}\bar{p}_{-1}p_{-1}(5)\bar{p}_0(6)f_9(r_5, r_6, r_{56})c_9^{-1}]\}\cdots,\end{aligned} \tag{20}$$

comes from a $\tilde{\chi}_1$, Eq. (8), which contains $\hat{u}_{ij}$'s for all the antiparallel spin correlations. But Eq. (20) is an eigenfunction only if the sets of variational parameters (divided by its c_i) in each function $f_i(r_5, r_6, r_{56})$ are all equal; e.g., each parameter of the set of parameters $\{\beta_{ki}/c_i, \alpha_{ki}/c_i\}$ of, say, $\hat{u}(2p_{+1}\alpha 2p_{-1}\beta)$ must be equal to the corresponding parameter in $\hat{u}(2p_{+1}\alpha 2p_{+1}\beta)$. This means that only a $\tilde{\chi}_1$ containing all antiparallel spin pair functions can be varied independently and that it essentially contains one set of independent variational parameters. These pair functions are coupled. Of course, with this $\tilde{\chi}_1$ the second-order energy is still the sum of $\bar{\epsilon}_{ij}^{(2)}$'s, Eq. (8), but each $\hat{u}_{ij}^{(1)}$ cannot be found by separate minimization of its $\bar{\epsilon}_{ij}^{(2)}$. This is so, simply because its parameters are not independent of those describing pair correlations in other parts of the system.

A $\tilde{\chi}_1$ with all antiparallel spin $\hat{u}_{ij}$'s is an eigenfunction of L^2, L_z, and S_z but not of S^2. To get an eigenfunction of L^2, L_z, S^2, S_z, we must add, to the above $\tilde{\chi}_1$, terms containing pair functions for all parallel spin correlations. There is again just one set of independent variational parameters for this complete $\tilde{\chi}_1$. This second set of terms is itself an eigenfunction of L^2, L_z, and S_z. The correlation energy for all the parallel spin pair correlations, i.e., six of them, will be much less than the antiparallel spin pair correlation energy due to the Fermi hole. Therefore, the coupling of pair functions due to S^2 requirements will be less than that expressed in Eq. (20). Some of the pair energies that are coupled will be equal. This reduces the effective number of pair energies that must be minimized simultaneously.

Our results are for pair functions $\hat{u}_{ij}^{(1)}$ in which i and j are HF orbitals, ϕ_i and ϕ_j. Putting interelectronic coordinates into the wavefunction through these $\hat{u}_{ij}$'s may give better convergence than CI, but many such $\hat{u}_{ij}$'s are coupled. Recall the expansion for αr_{12}:

$$\alpha r_{12} = \sum_{l=0}^{\infty} \alpha f_l(r_1, r_2) P_l(\cos\theta_{12}). \tag{21}$$

[6] A bar over the function indicates a β spin eigenfunction.

The Legendre polynomial, $P_l(\cos\theta_{12})$, can be written in terms of spherical harmonics for θ_1, ϕ_1 and θ_1, ϕ_2. This αr_{12} then introduces all the spherical harmonics, $s, p, d, f, \cdots$ into the wavefunction with equal weight, α. Selectively picking terms out of the expansion, Eq. (21) could be used to reduce the coupling between pair functions. One may also start with a two-electron function which, besides satisfying all the orthogonality requirements of a $\hat{u}_{ij}$, has definite symmetry properties.[7] Such pair functions can be called symmetry pair functions. These pair functions must have ^1S, ^1D, or ^3P symmetry and will be coupled to the ^1S, ^1D, or ^3P multiplets of the $(2p)^4$ configuration. But these symmetry pair functions can be shown to contain, in effect, many ordinary $\hat{u}_{ij}$'s plus some other terms; e.g., for the ^1S pair there are nine such terms. Thus, symmetry pairs should not bring about much simplification.

CONCLUSIONS

We have examined the angular-momentum properties of a correlation wavefunction built up from pair functions $\hat{u}_{ij}$. These $\hat{u}_{ij}$ functions describe the correlation between electrons in HF orbitals ϕ_i and ϕ_j. There is one such function for each pair of electrons. With a first-order wavefunction of this type, Eq. (8), the second-order energy reduces to a sum of pair energies,[8] $\sum_{i>j}\tilde{\epsilon}_{ij}{}^{2)}$.

Each $\hat{u}_{ij}{}^{(1)}$ can be found by separate minimization of its pair energy $\tilde{\epsilon}_{ij}{}^{(2)}$ [Eq. (9)], provided the resulting wavefunction has the correct symmetry properties; e.g., for atoms it must be an eigenfunction of the orbital and spin angular momentum operators. If we can take a part of $\tilde{\chi}_1$ containing just one $\hat{u}_{ij}{}^{(1)}$ and obtain this $\hat{u}_{ij}{}^{1)}$ variationally by minimizing its $\tilde{\epsilon}_{ij}{}^{2)}$ so that $\tilde{\chi}_1$ has the correct symmetry properties, then this $\hat{u}_{ij}{}^{(1)}$ is independent, i.e., uncoupled.[8] If not, we must work with a $\tilde{\chi}_1$, containing enough pair functions, so as always to have the right symmetry when its $\hat{u}_{ij}{}^{(1)}$'s are varied. We have examined these properties of the pair functions for the $2p^n$ electrons of $C(^3P, ^1D, ^1S)N(^4S)$, $O(^3P)$, and Ne. The $\hat{u}_{ij}{}^{(1)}$'s contain quite general powers of electronic and interelectronic coordinates and are sufficient for our purposes.

The $2p^2$ system, with only one pair of electrons, is a special case. There are no restrictions on the $\hat{u}(2p^2)$ of the ^3P multiplet. In the ^1D multiplet, for the $\hat{u}(2p^2)$ to contain arbitrary powers of the interelectronic coordinate it must be orthogonalized not only to the occupied orbitals of the open shell but also to the unoccupied ones. This is a symmetry requirement that can be expressed as an orthogonality requirement and has not been obvious. The term containing $r_{12}{}^2$ is an exception to this. We apply the angular-momentum step-down operator to these correlation wavefunctions of multiplet states with single Slater determinant Hartree–Fock wavefunctions and get the corresponding form of the correlation wavefunctions for the non-single-determinant HF states of these multiplets. From these we can infer the correlation wavefunction for the ^1S multiplet which does not have a single-determinant HF wavefunction.

For $2p^3(N, ^4S)$, $2p^4(O, ^3P)$, and $2p^6(Ne)$, we have shown that our correlated pair functions [see Eq. (11)] are not independent. To obtain a correlation wavefunction variationally, it must contain pair functions for all the pair correlations of the system since the variational parameters in one such function are not independent of these in the others. The set of variational parameters divided by c (c is itself a function of these parameters) [see Eq. (12)] must be the same for all the pair functions. For the $2p^3$ electrons of N, we must deal variationally with a $\tilde{\chi}$ containing three $\hat{u}_{ij}{}^{(1)}$'s and only the sum of their pair energies, $\sum_{i>j}\tilde{\epsilon}_{ij}{}^{(2)}$, can be minimized. For the $(2p)^6$ electrons of Ne, we can only rigorously minimize the sum of fifteen such pair energies all at once and cannot deal with just one pair energy at a time. Only in this way will the correlation wavefunction "belong" to the Ne atom. These fifteen pair energies can be divided into two groups, one of nine and the other of six pair energies, which should be only weakly coupled. These groups correspond to the antiparallel and parallel spin pair correlation energies. This coupling of the various pair correlation functions through symmetry requirements will now make the determination of pair correlation functions quite a bit more difficult.

[7] A. Lowrey (private communication) is attempting such a formulation.

[8] With the first-order wavefunctions we are not concerned with coupling through three-body effects.